Journal of Analytical and Applied Pyrolysis 111 (2015) 121–131

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Analytical pyrolysis of hot water pretreated forest biomass

Étienne Le Roux[a], Papa Niokhor Diouf[b], Tatjana Stevanovic[a,*]

[a] Centre de Recherche sur les Matériaux Renouvelables, Department of Wood and Forest Science, Faculty of Forestry, Geography and Geomatic, Laval University, Pavillon Gene-H.-Kruger, 2425 Rue de la Terrasse, G1V 0A6 Quebec, QC, Canada
[b] Service de recherche et d'expertise en transformation des produits forestiers (SEREX), 25 rue Armand-Sinclair, porte 5, G5J 1K3 Amqui, QC, Canada

ARTICLE INFO

Article history:
Received 2 June 2014
Accepted 28 November 2014
Available online 4 December 2014

Keywords:
Pyrolysis–gas chromatography/mass spectrometry
Pressurized Hot Water Treatment
Wood biomass
Fast pyrolysis
Bio-oil

ABSTRACT

Fast pyrolysis is a promising technology to promote wood biomass utilization. This thermochemical process produces mainly a liquid bio-oil. Currently, a direct application of bio-oil as fuel is limited due to its poor physicochemical properties.

Pressurized Hot Water Treatment (PHWT) has been applied on white spruce and trembling aspen whole wood chips prior to production of pyrolysis oil. The effect of PHWT and the influence of the fast pyrolysis parameters on the bio-oil composition and products distribution were investigated by analytical pyrolysis coupled with gas chromatography/mass spectrometry (Py–GC/MS), it was carried out at two heating rates (100 °C/min and 1000 °C/min) and in temperature ranges from 350 °C to 500 °C for trembling aspen and from 400 °C to 550 °C for white spruce. The pyrolysis products were identified to belong to eleven chemical groups: syringyl derivatives, guaiacyl derivatives, other phenolics, anhydrosugars, low molecular weight acids, fatty acids, furans, pyrans, ketones, aldehydes and alcohols.

The results of the analytical pyrolysis indicate that the higher yield is obtained from pretreated than from untreated biomass. The effect of the pretreatment is more important for the 1000 °C/min heating rate than for 100 °C/min. The composition analysis revealed that the higher peak area% of anhydrosugar were obtained from PHWT biomass at 1000 °C/min while the phenols were the major constituents of the pyrolysis products obtained at lower, 100 °C/min heating rate. It is also demonstrated that the acids are still found in pyrolysis products even after pretreatment. The Py–GC/MS results obtained in this study indicate that pretreatment affected the hardwood and softwood in quite different ways.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The world energy consumption has considerably risen during the last forty years and the same trend will remain until 2035 according to the International Energy Agency [1]. Amongst the energy resources, fossil fuels are predominant. Nevertheless the future depletion of fossil resources, the high costs of petroleum, the global warming, and the energy security issues require decreasing the oil dependence. It is therefore urged to replace fossil fuels by more eco-friendly resources. Biomass represents one of the alternatives, since it is a renewable, abundant and low cost resource. It is already used by the pulp and paper industry as a feedstock for chemicals and fuels. Forest biomass transformation into bio-oil can offer some solutions to this industry which is presently facing one of its most important crises.

Various forms of woody biomass are available from wood processing such as sawdust, barks, branches, twigs, etc. The research has been focused on the integration of woody biomass valorization in an integrated biorefinery process [2]. Fast pyrolysis is one of the most promising technologies to promote woody biomass valorization [3,4]. Pyrolysis is a thermochemical degradation occurring in an inert atmosphere. It produces mainly 60–75 wt% of a liquid bio-oil, 15–25 wt% of biochar and 10–20 wt% of non-condensable gas [5]. The bio-oil could be a valuable feedstock for chemical production or fuels. However the bio-oil is a complex mixture. Its chemical composition and distribution depend on the origin of the biomass and the parameters of the pyrolysis. The main constituents of a crude bio-oil originate from the thermal decomposition of three principal components of lignocellulosic biomass, hemicelluloses, cellulose and lignins. Crude bio-oil composition is well studied by several analytical tools such as GC/MS [6] and it could be resumed to: 30% water, 30% phenolics, 20% aldehydes and ketones, 10% alcohols and 10% others compounds [7]. Due to its composition, the crude bio-oil presents some physical properties which

---

* Corresponding author. Tel.: +1 418 656 2131x7337; fax: +1 418 656 2091.
E-mail address: Tatjana.Stevanovic@sbf.ulaval.ca (T. Stevanovic).

http://dx.doi.org/10.1016/j.jaap.2014.11.023
0165-2370/© 2014 Elsevier B.V. All rights reserved.

impede its direct application. Indeed, the degradation products of carbohydrates, particularly those from hemicelluloses, give an acidic character to the bio-oil (pH around 2–3). The thermal degradation generates also other oxygenated compounds. They are susceptible to react during storage and transport operations. The viscosity of the bio-oil may thus be modified. Moreover, the water content reduces the heating value of the bio-oil.

To eliminate these drawbacks, a pretreatment of the biomass is one of the solutions proposed in the literature [8,9]. In our previous work [10], two woody biomasses, trembling aspen (*Populus tremuloides*) and white spruce (*Picea glauca*), were torrefied in the presence of water in a pressure vessel. Chemical, proximate and elementary analyses were performed on the pretreated wood and the harsher the pretreatment, the higher reduction of hemicelluloses content was determined. At the same time, a partial solubilization of lignins was observed for the hardwood. These alterations of the feedstock would certainly modify the chemical composition and distribution of the constituents in the bio-oil produced. Py–GC/MS analysis is an appropriate analytical technique for investigation of the thermal behavior of a biomass. The Py–GC/MS technique is combining an analytical pyroprobe with a gas chromatograph coupled with a mass spectrometer. This analytical technique is used to achieve biomass fast pyrolysis and allows on-line analysis of the pyrolysis products in order to get information on their distribution.

Despite the fact that the Py–GC/MS analysis of untreated wood is well documented, there are only a few studies on pretreated wood analyses [11,12]. This study is focusing on the thermochemical behavior of the pretreated biomass during a fast pyrolysis. The Py–GC/MS analyses were performed at two heating rates, 100 °C/min and 1000 °C/min, corresponding to the heating rates commonly applied in fast pyrolysis. The experiments were carried out applying the parameters simulating common conditions of woody biomass fast pyrolysis with an aim to investigate the effect of a PHWT pretreatment on the chemical composition and the distribution of the constituents.

2. Experimental

2.1. Wet torrefied biomass production

Two woody biomasses were studied, hardwood trembling aspen (*P. tremuloides*) and softwood white spruce (*P. glauca*). The wood chips, produced from whole logs without debarking, were obtained from Groupe BSL sawmill located in Amqui, Quebec, Canada. They were received oven dried to 8% moisture content. The wood samples were subjected to a PHWT pretreatment in a 2 L stirred pressure reactor (Parr 4522) at 175 °C, 195 °C and 215 °C. A severity factor, *S*, was calculated taking into account the time (*t*) and the pretreatment temperature (*T*) [13,14] as explained by Eqs. (1) and (2) in which TREF is 373 K:

$$S = \log R \tag{1}$$

$$R = \int_0^t \exp\left(\frac{T - \mathrm{TREF}}{w}\right) dt \tag{2}$$

Thus, for PHWT performed at 175 °C, 195 °C and 215 °C, the severity factors were calculated to be 3.9, 4.6 and 5.2 [10]. The results of chemical analysis of untreated and pretreated wood [10] are presented in Table 1.

The solid residues were collected, washed with hot water (1 L), and air dried. The pretreatment was triplicated for each severity. Prior to pyrolysis analysis, the pretreated and untreated wood chips, were successively milled in a cutting mill (Pulverisette 19, Fritsch), and in a hammer mill (Mikrom-Batam) in order to obtain sawdust with a particle size under 1 mm.

2.2. Pyrolysis–gas chromatography/mass spectrometry

The analytical pyrolysis was performed using a CDS Pyroprobe 2000 heated coil pyrolyzer. The fast pyrolysis was performed at 350 °C–400 °C–450 °C–500 °C and 400 °C–450 °C–500 °C–550 °C for trembling aspen and white spruce, respectively, and held at these temperatures for 3.0 min. Two heating rates were selected, 100 °C/min and 1000 °C/min. These rates were chosen to study the fast pyrolysis process under its entire heating rate range. The organic volatile species were analyzed in a GC/MS system (Varian CP-3800, Varian Saturn 2200). The pyrolysis products were separated in capillary column VF-5 ms (30 m × 0.25 mm × 0.25 μm inner diameter). Helium was the carrier gas with a flow rate of 1 mL/min. About 1 mg of biomass sample was pyrolyzed at 100 °C/min with a split ratio of 50:1. The experiments at the heat rate of 1000 °C/min were first performed with the same parameters but some compounds, particularly sugars, seemed to stick to the column. Therefore, the sample weight and the split ratio were changed respectively to 0.15 mg and 100:1 for the heating rate of 1000 °C/min. The column oven program was: 9 min and 4 min at 45 °C for the heating rate of 100 °C/min and 1000 °C/min respectively, followed by an increase to 280 °C (5 °C/min) and hold at that temperature for 10 min. The gases were then sent into a mass spectrometer operating in Electron Ionization mode at 70 eV. The mass spectra were obtained from *m*/*z* 40 to 400 with a scan rate of 1 scan/s. The identification of the chromatographic peaks was based on the NIST library and on the data available in the literature [15–18]. All samples, untreated wood samples and triplicates samples from each pretreatment severity were pyrolyzed twice.

When analysis the Py–GC/MS results only the relevant part of the chromatogram was considered. Indeed, the compounds detected after the retention times of 45 min and 40 min for the pyrolysis performed at 100 °C/min and 1000 °C/min heating rates, were considered as irrelevant. They were not related to the thermal degradation of lignocellulosic biomass but to the Py–GC/MS analysis system. Thus, the calculations concerned only peaks detected before these retention times.

For each identified compound, the peak area values and the peak area% were normalized per mg of sample dry weight and used for discussion. The peak area value of a compound which is considered to be proportional to its concentration is used to discuss the changing of its yields under different pyrolysis conditions [19,20]. The peak area% of a product is used to discuss the changing of the compound distribution under different pyrolysis conditions.

3. Results and discussions

Fig. 1 present an example of pyrogram of untreated trembling aspen pyrolyzed at 450 °C with a heating rate of 1000 °C/min. Biomass fast pyrolysis products are composed of permanent gases and condensable gases which consist of water, volatile compounds and non-volatile oligomers which will form bio-oil after condensation [19]. During the condensation, recombination reactions between the products may also occur. In the case of an analytical Py–GC/MS, the organic condensable products are separated thus avoiding recombination reactions instead of being collected in the form of bio-oil as is the case for fast pyrolysis. Only monomers and few dimers are detected by the mass spectrometer. Therefore, the compounds identified by Py–GC/MS analysis represent only a fraction of the real constituents of the bio-oil which will be produced by pyrolysis from the studied biomass. Nevertheless, this analysis helps to estimate the yield change under different pyrolysis conditions and predict the chemical distribution of the pyrolysis products. The compounds identified from pyrolysis are classified into nine chemical groups, including phenolics,

Table 1
Chemical composition of wood biomass pretreated under different PHWT conditions (wt% ± standard deviation%) [9].

Biomass	Severity	Hemicelluloses	Cellulose	Lignins
Trembling aspen	0	23.4 ± 0.4	52.2 ± 0.0	24.4 ± 0.4
	3.9	19.4 ± 0.5	57.7 ± 0.2	22.9 ± 0.2
	4.6	8.0 ± 0.9	72.0 ± 0.6	20.0 ± 0.3
	5.2	4.0 ± 1.2	78.4 ± 0.8	17.6 ± 0.3
White spruce	0	16.8 ± 0.2	53.6 ± 0.2	29.6 ± 0.0
	3.9	13.4 ± 0.4	56.5 ± 0.1	30.1 ± 0.3
	4.6	6.1 ± 0.4	59.8 ± 0.1	34.1 ± 0.3
	5.2	0.7 ± 0.5	63.5 ± 0.2	35.9 ± 0.2

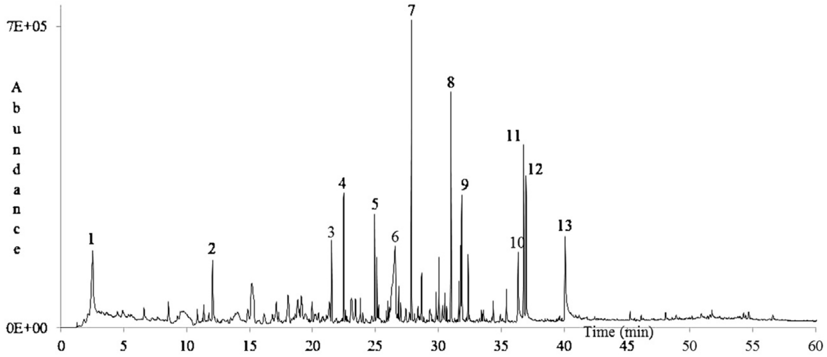

Fig. 1. Chromatogram of trembling aspen pyrolysis products obtained from Py–GC/MS performed at heating rate of 1000 °C/min and 450 °C.

anhydrosugars, low molecular weight acids, fatty acids, furans, pyrans, ketones, aldehydes and alcohols. The phenolics are derived from the lignin pyrolysis and can be subdivided into molecules with syringyl, guaiacyl, and other aromatics moieties. The anhydrosugars, the pyrans, and the furans are generated from the thermal degradation of holocellulose. The fatty acids are related to the pyrolysis of wood extractives.

One of the drawbacks of the Py–GC/MS analysis is that the standard deviations could be very large. That has already been reported previously in the literature [21,22]. The low sample mass introduced in the pyroprobe, the particle size and the inhomogeneity of the samples studied here due to the presence or absence of bark could explain the high variability of the obtained results. In order to evaluate the Py–GC/MS results, an ANOVA analysis (95% confidence interval) was performed for each Py–GC/MS replicate on the total peak area values and the peak area% of each chemical family and for each heating rate. The results from the two wood species were examined separately. The peak area% of some specific pyrolysis products were analyzed as well. The significant (+) or non-significant (−) effects of pretreatment severity and of pyrolysis temperature were determined based on the peak area values and the peak area% obtained from the Py–GC/MS performed at 100 °C/min and at 1000 °C/min heating rates, as presented in Tables 2a and 2b, respectively.

3.1. *Effect of pyrolysis operating conditions on pyrolysis yields*

3.1.1. *100 °C/min pyrolysis*

At slow heating rate of 100 °C/min, it seems that the same or higher quantities of pyrolysis products were produced from untreated aspen than from pretreated samples and that at all examined pyrolysis temperatures. The highest production is observed for a pyrolysis performed at 450 °C. For spruce, neither the severity pretreatment nor the pyrolysis temperatures seem to have a significant effect.

These results showed that the PHWT pretreatment could not increase the yield of pyrolysis products in case of a pyrolysis performed at 100 °C/min.

3.1.2. *1000 °C/min pyrolysis*

The results of average total peak area values from the 1000 °C/min pyrolysis are given in Fig. 2a and b for aspen and spruce, respectively.

The total peak area values for the products issued from pyrolysis performed at heating rate of 1000 °C/min are ten times higher than the results obtained for the heating rate of 100 °C/min. A high heating rate seems to lead to a more advanced thermal degradation of biomass. The quantity of pyrolysis products is increased. Consequently, the fast pyrolysis performed at high heating rate does enhance the pyrolysis yield.

Since the lower total peak area values are determined at lower temperatures, the pyrolysis operating temperature should be higher than 350 °C and 400 °C respectively for hardwood and

Table 2a
Results of the ANOVA analysis performed on the total peak area value and the area% of each chemical family obtained from the Py–GC/MS carried out at 100 °C/min. Significant effect (+), non significant effect (–).

Biomass	PHWT	Pyrolysis temperature
Trembling aspen		
Total peak area values	+	+
Peak area% of phenolics	+	–
Peak area% of fatty acids	–	+
Peak area% of furans	–	+
Peak area% of 3-MFD		
Peak area% of 5-HMF		
Peak area% of anhydrosugars	+	+
White spruce		
Total peak area values	–	–
Peak area% of phenolics	+	–
Peak area% of fatty acids	–	+
Peak area% of furans	+	+
Peak area% of anhydrosugars	+	–

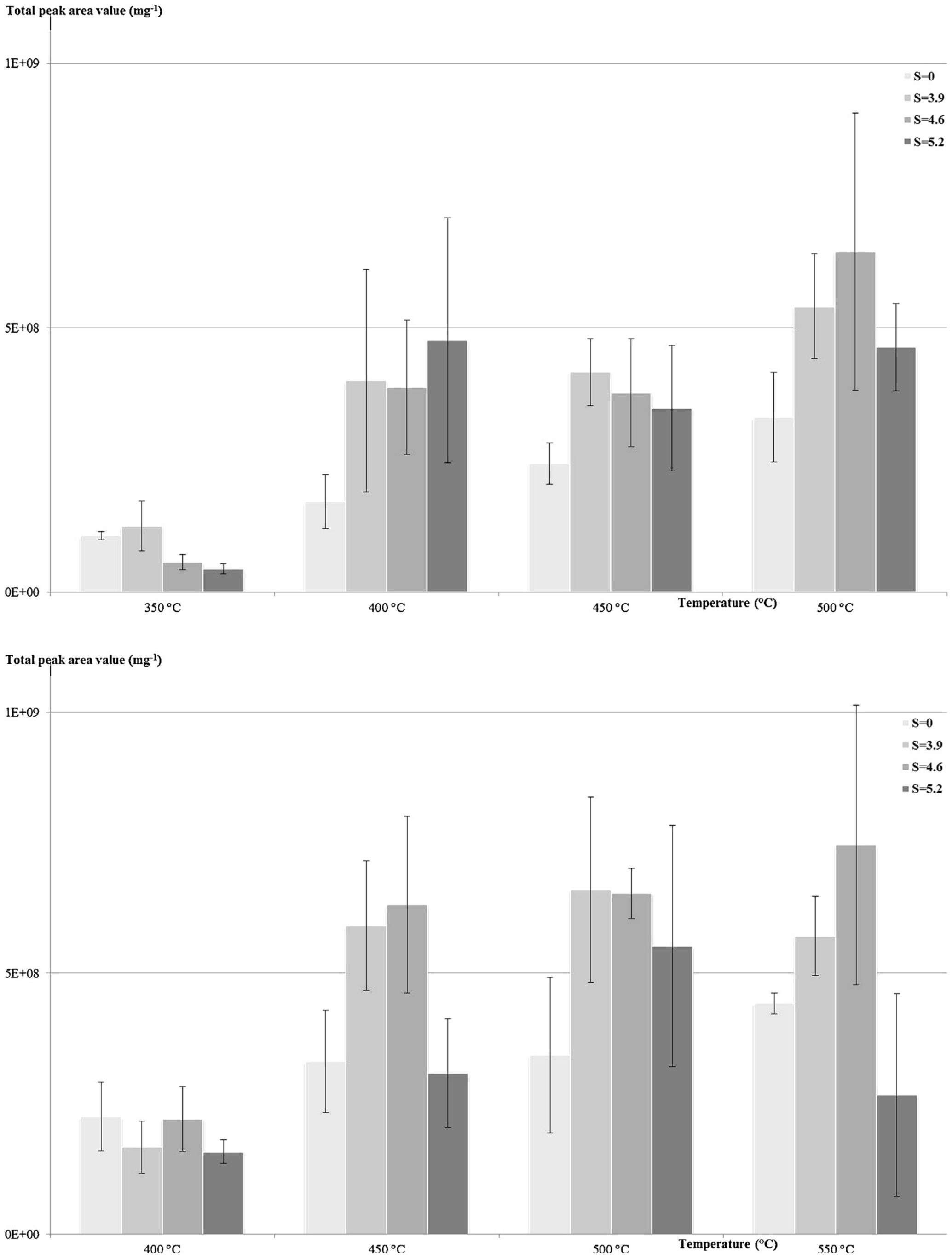

Fig. 2. (a) Total peak area values for PHWT trembling aspen ($S = 0$ – untreated; $S = 3.9$ pretreated at 175 °C; $S = 4.6$ at 195 °C and $S = 5.2$ at 215 °C) fast pyrolyzes performed at heating rate of 1000 °C/min and temperatures 350 °C, 400 °C, 450 °C and 500 °C. (b) Total peak area values for PHWT white spruce ($S = 0$ – untreated; $S = 3.9$ pretreated at 175 °C; $S = 4.6$ at 195 °C and $S = 5.2$ at 215 °C) fast pyrolyzes performed at heating rate of 1000 °C/min and temperatures 400 °C, 450 °C, 500 °C and 550 °C.

softwood. The results similar to those obtained for aspen have been reported previously for poplar [19].

The total peak area values corresponding to pyrolysis products released from untreated biomass increase regularly with the increase of pyrolysis temperature. In the case of pretreated aspen, except for the lowest temperature, at a given pyrolysis temperature, the pretreated aspen produces more pyrolysis products than the untreated aspen. The highest total peak area values were obtained at 500 °C. In the case of pretreated spruce, the total peak area values increased with the increase of pyrolysis temperature for temperatures above 400 °C, especially high yield determined at 500 °C and 550 °C. However, the harsh pretreatment conditions ($S = 5.2$) seem to reduce the yield of pyrolysis products. Indeed at every pyrolysis temperatures, pretreated spruce at $S = 5.2$ appears to give almost the same yield of pyrolysis products than untreated spruce. This could be explained by the fact that at $S = 5.2$, all hemicelluloses had been removed from spruce which could explain the decrease in yield of pyrolysis products (Fig. 2b).

It seems that the yield of pyrolysis products is greatly improved by the pretreatment when the pyrolysis is performed at a high heating rate. The high pyrolysis temperature, 500 °C and 550 °C, affects also the results. The severity of the pretreatment seems to influence the production of pyrolysis compounds, and particularly so in the case of trembling aspen pretreated at the highest $S = 5.2$.

Table 2b
Results of the ANOVA analysis performed on the total peak area value and the area% of each chemical family obtained from the Py–GC/MS carried out at 1000 °C/min. Significant effect (+), non significant effect (−).

Biomass	PHWT	Pyrolysis temperature
Trembling aspen		
Total peak area values	+	+
Peak area% of phenolics	+	+
Peak area% of syringol derivatives	+	+
Peak area% of guaiacol derivatives	+	+
Peak area% of fatty acids	−	−
Peak area% of furans	+	+
Peak area% of anhydrosugars	+	+
Peak area% of acids	+	−
Peak area% of acetic acid		
White spruce		
Total peak area values	+	+
Peak area% of phenolics	−	+
Peak area% of fatty acids	+	+
Peak area% of furans	+	+
Peak area% of anhydrosugars	+	+
Peak area% of acids	+	+
Peak area% of acetic acid	+	+

Table 3
List of identified compounds from a Py–GC/MS performed at rate of 1000 °C/min and 450 °C on trembling aspen sample.

Number	Compounds	R.T. (min)	Peak area%
1	Acetic acid	2.5	4.7
	Furan-2-carbaldehyde	6.6	0.3
	5-Hydroxymethyl dihydrofuran-2-one	8.5	0.6
	cyclopentanedione	9.5	0.4
	3-Acetyl dihydro-2(3H)-furanone	10.8	0.4
	phenol	11.3	0.6
	2H-pyran-2,6(3H)-dione	11.8	0.4
2	3-Methyl-2,4(3H,5H)-furandione	12.1	1.7
	2-Methoxy-phenol	14.8	0.6
	Unidentified anhydrosugars	15.2	3.6
	2-Methoxy-2,3-dihydro-furan-3-carboxaldehyde	16.8	0.4
	Benzoic acid	17.1	1.0
	2,3-Dihydroxy-benzaldehyde	17.3	0.4
	2-Methoxy-4-methyl-phenol	18.1	1.6
	3-Hydroxy-cyclohexanone?	18.9	0.5
	5-Hydroxymethyl-2-furancarboxaldehyde	19.1	1.5
	3-Methoxy-1,2-benzendiol	20.0	0.7
	4-Ethyl-2-methoxy-phenol	20.5	0.4
	3-Methyl-2-pentanol	20.7	0.1
	4-Methyl-1,2-benzendiol	20.8	0.3
3	4-Vinyl-2-methoxy-phenol	21.5	1.9
4	2,6-Dimethoxy-phenol	22.5	2.3
	2-Methoxy-4-(2-propenyl)-phenol	22.6	0.2
	3,4-Dimethoxyphenol	22.7	0.2
	Benzenetriol	23.1	1.5
	4-Hydroxy-3-methoxybenzaldehyde	23.8	0.5
	2,5-Dihydroxy-benzeneacetic acid	24.7	0.2
5	4-Hydroxy-3-methoxy benzoic acid	24.9	1.8
	2-Methoxy-4-(prop-1-en-1-yl)phenol	25.1	1.1
	2-Methoxy-4-propylphenol	25.2	0.5
	6-Methoxy-3-methylbenzofuran	25.9	0.2
	1-(4-Hydroxy-3-methoxyphenyl)-ethanone	26.0	0.4
6	(1*R*,2*S*,3*S*,4*R*,5*R*)-6,8-Dioxabicyclo[3.2.1]octane-2,3,4-triol	26.5	7.3
	4-Ethyl-2,6-dimethoxyphenol	26.8	0.8
	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	27.0	0.4
	2-Methoxy-alpha,5-dimethyl-benzeneacetaldehyde	27.7	0.3
7	1-(3,4-Dimethoxyphenyl)ethanone	27.9	5.0
	2,6 Dimethoxy-4-(2-propenyl)-phenol	28.7	1.0
	4-Hydroxy-3-methoxy benzene acetic acid	29.8	0.6
	4-Hydroxy-3,5-dimethoxybenzaldehyde	30.0	1.2
	4-(3-Hydroxy-1-propenyl)-2-methoxyphenol	30.3	0.5
	7-Methoxybenzofuran-2-carboxylic acid	30.5	0.6
	4-(4-Hydroxy-3-methoxyphenyl)-3-buten-2-one	30.7	0.3
8	2,6-Dimethoxy-4-(prop-1-enyl)phenol	31.0	3.8
	1-(4-Hydroxy-3,5-dimethoxyphenyl) ethanone	31.6	0.6
	4-Hydroxy-3-methoxycinnamaldehyde	31.7	1.1
9	4-(3-Hydroxy-1-propenyl)-2-methoxyphenol	31.8	2.7
	Tetradecanoic acid	32.2	0.1
	1-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanone	32.4	1.1
	1,4,5-Trimethoxy-benzyl ether	32.5	0.2
	2,5-Dimethoxy-benzenemethanol acetate	33.4	0.3
	4-Phenyl propiophenone	33.6	0.4
	1-(3-Methoxy-methyl)-2,4,6-trimethyl phenyl)-ethanone	33.8	0.1
	bis(2-Methylpropyl) ester 1,2-benzenedicarboxylic acid	34.4	0.5
	3,5-Dimethoxy-4-hydroxyphenylacetic acid	34.9	0.2
	4-(3-Hydroxyprop-1-enyl)-2,6-dimethoxyphenol	35.4	0.9
10	Hexadecanoic acid	36.3	2.3
11	3,5-Dimethoxy-4-hydroxycinnamaldehyde	36.8	3.4
12	4-(3-Hydroxyprop-1-enyl)-2,6-dimethoxyphenol	37.0	4.9
13	Octadecanoic acid	40.1	4.0

3.2. *Effect of pyrolysis operating conditions on chemical distribution of pyrolysis products*

It is noteworthy that for a given Py–GC/MS analysis (with defined PHWT severity and pyrolysis temperature) the sum of the peak area% was never 100%. Indeed, in the retention times of the chromatogram used for the calculations (between 0 min and 45 min for the pyrolysis performed at 100 °C/min heating rate and between 0 min and 40 min at 1000 °C/min heating rate) some peaks remain unidentified on the total ion chromatogram as can be seen in Fig. 1 and in Table 3.

An example of chromatogram is given in Fig. 1 and the peaks numbered 1–13 are identified in Table 3 in which the pyrolysis products identified with retention times and peak area%.

The chemical compositions of pyrolysis products of Py–GC/MS analysis performed at heating rates of 100 °C/min and at 1000 °C/min are presented in Tables 4 and 5 respectively.

The identification of pyrolysis products reveals that there are twice more different compounds identified among pyrolysis products released from woody biomass heated at higher rate of 1000 °C/min than at 100 °C/min. The chemical diversity of the pyrolytic products is therefore enhanced by an increase of heating rate. Moreover, it is important to note that under a slow heating rate the diversity of chemical composition is higher for aspen than for spruce (Table 4).

3.2.1. *Phenolics*

Phenolics are derived from the thermal degradation of lignin. In this study, phenolics obtained after analytical pyrolysis were classified into three fractions: guaiacol derivatives (guaiacol, 4-methyl guaiacol, 4-vinyl guaiacol, vanillic acid, isoeugenol, acetoveratrone, coniferyl aldehyde, coniferyl alcohol), syringol derivatives (syringol, syringaldehyde, allyl syringol, acetosyringone, sinapaldehyde, sinapyl alcohol) and other phenolics (phenol, benzenediol).

For the pyrolysis performed at heating rate of 100 °C/min, phenolics are the main pyrolysis products, accounting for 50% of all compounds or more for both hardwood and softwood. According to the results of ANOVA analysis (Table 2a), the temperature of pyrolysis has not significant influence on the peak area% of phenolics compounds neither for aspen nor for spruce pyrolysis. As for the pyrolysis of PHWT, only wood pretreated at the highest severity ($S = 5.2$) presents a peak area% of phenolics higher than that of untreated wood and it was only the case for pyrolysis temperatures of 350 °C and 450 °C for aspen and spruce, respectively. For

Table 4
Composition of the pyrolysis products obtained at the heating rate of 100 °C/min under different pyrolysis conditions from pretreated trembling aspen (TA) and from white spruce (WS) (average peak area% ± standard deviation%).

Temperature (°C)	Severity	Relative peak area ratio% ± SD%						
		Phenols	Fatty Acids	Acids	Anhydrosugars	Furans	Pyrans	Other
TA								
350	0	44.6 ± 9.2	9.2 ± 5.5	1.1 ± 0.5	1.1 ± 0.3	6.3 ± 1.4	1.6 ± 0.4	1.6 ± 0.3
	3.9	43.6 ± 8.7	11.0 ± 3.2	1.4 ± 1.1	1.6 ± 0.3	5.6 ± 1.6	3.2 ± 1.0	2.4 ± 0.6
	4.6	52.9 ± 8.4	11.6 ± 7.9	2.6 ± 1.4	1.7 ± 1.0	3.9 ± 1.7	2.7 ± 0.9	0.7 ± 1.1
	5.2	61.0 ± 13.8	5.4 ± 4.3	0.7 ± 0.7	0.6 ± 0.4	2.1 ± 0.4	3.6 ± 2.4	1.0 ± 0.9
400	0	49.6 ± 1.6	2.4 ± 0.7	0.4 ± 0.4	1.5 ± 0.1	5.0 ± 0.6	1.6 ± 0.9	1.6 ± 0.2
	3.9	48.7 ± 7.2	3.6 ± 0.6	0.2 ± 0.2	2.9 ± 0.8	6.9 ± 3.3	1.7 ± 0.7	1.1 ± 0.8
	4.6	56.4 ± 4.1	4.7 ± 0.8	0.9 ± 0.7	2.4 ± 0.9	5.9 ± 1.5	1.7 ± 0.9	1.0 ± 0.6
	5.2	56.5 ± 9.9	7.1 ± 3.4	0.6 ± 0.7	1.0 ± 0.4	6.5 ± 1.9	0.5 ± 0.3	0.5 ± 0.3
450	0	42.6 ± 5.5	4.4 ± 2.2		1.2 ± 0.2	6.3 ± 0.8	0.7 ± 0.1	2.4 ± 0.9
	3.9	51.3 ± 7.6	4.0 ± 0.9		2.0 ± 0.6	7.0 ± 2.0	1.5 ± 0.6	2.0 ± 0.7
	4.6	52.1 ± 9.1	3.2 ± 1.2		1.3 ± 0.4	5.8 ± 1.1	0.7 ± 0.4	1.6 ± 1.1
	5.2	53.8 ± 9.0	3.8 ± 1.6		1.4 ± 0.7	7.8 ± 1.8	1.7 ± 1.3	1.5 ± 1.2
500	0	52.4 ± 3.0	1.7 ± 0.0		0.7 ± 0.3	5.3 ± 3.2	0.8 ± 0.0	2.1 ± 0.7
	3.9	53.1 ± 3.5	2.5 ± 1.0		4.9 ± 2.5	6.6 ± 2.3	2.2 ± 0.5	2.0 ± 1.1
	4.6	52.5 ± 8.7	3.5 ± 1.0		3.2 ± 0.8	6.5 ± 2.0	0.6 ± 0.2	1.3 ± 1.1
	5.2	50.2 ± 4.6	3.3 ± 1.2		3.5 ± 1.0	7.2 ± 0.8	1.0 ± 0.6	1.1 ± 0.8
WS								
400	0	48.3 ± 5.5	3.4 ± 0.5		2.0 ± 0.1	6.5 ± 0.8		0.4 ± 0.1
	3.9	49.1 ± 9.9	3.0 ± 1.0		2.3 ± 1.2	8.9 ± 1.9	0.5 ± 0.1	0.4 ± 0.3
	4.6	44.4 ± 4.4	2.1 ± 1.3		1.0 ± 1.0	7.5 ± 1.5		0.3 ± 0.3
	5.2	51.2 ± 8.2	4.5 ± 2.1		4.5 ± 1.9	12.0 ± 1.8		0.3 ± 0.5
450	0	47.5 ± 4.4	5.6 ± 1.3		2.2 ± 0.6	5.4 ± 0.1		0.8 ± 0.0
	3.9	50.1 ± 9.7	4.1 ± 1.7		4.2 ± 2.0	7.3 ± 1.4	0.5 ± 0.2	0.6 ± 0.6
	4.6	45.0 ± 4.5	3.3 ± 1.5		2.7 ± 1.3	8.8 ± 1.4		0.1 ± 0.6
	5.2	57.8 ± 6.8	3.1 ± 1.2		4.1 ± 2.2	10.6 ± 1.9		0.2 ± 0.3
500	0	42.3 ± 3.5	2.4 ± 1.7		1.6 ± 0.1	4.0 ± 0.2		0.8 ± 0.1
	3.9	49.1 ± 7.5	4.6 ± 4.1		2.8 ± 1.4	6.5 ± 2.4		0.5 ± 0.4
	4.6	49.7 ± 6.1	3.2 ± 1.7		3.0 ± 0.7	7.8 ± 0.6		0.6 ± 0.2
	5.2	50.1 ± 6.3	3.9 ± 3.4		4.8 ± 1.6	7.4 ± 1.8		0.4 ± 0.3
550	0	43.9 ± 4.4	1.9 ± 0.5		1.0 ± 0.0	4.4 ± 0.1		0.7 ± 0.2
	3.9	48.4 ± 6.7	2.8 ± 1.7		1.8 ± 0.7	6.3 ± 1.3		0.4 ± 0.4
	4.6	51.7 ± 8.7	3.0 ± 1.5		3.7 ± 1.6	8.3 ± 0.9		0.5 ± 0.4
	5.2	51.0 ± 10.1	2.9 ± 2.6		5.4 ± 1.5	8.3 ± 2.2		0.5 ± 0.3

the rest, it seems that PHWT wood displays a peak area% of phenolics comparable to the peak area% of phenolics issued by pyrolysis from untreated wood. Thus, at low heating rate, the pretreatment does not have an effect on the peak area% of phenolics.

At heating rate of 1000 °C/min, phenolics are still predominant pyrolysis products but with lower relative importance than for the pyrolysis performed at 100 °C/min heating rate. The phenolics peak area% decreased with the increase of pyrolysis temperature especially for the highest pyrolysis temperature, 500 °C for aspen and 550 °C for spruce. Regarding the pretreatment, it seems that the peak area% of phenolics issued by pyrolysis from PHWT at $S = 5.2$ decreased in the case of aspen, while for spruce, the PHWT does not seem to have significant effect according to the ANOVA analysis (Table 2b).

The phenolic compounds from aspen pyrolysis are mainly composed of syringyl (S) and guaiacyl derivatives (G) [16]. The development of ratio S/G according to the severity of the pretreatment and the pyrolysis temperatures of trembling aspen is shown in Fig. 3.

Like it was previously observed [16], the peak area% of syringyl derivatives is higher than that of guaiacyl derivatives for low pyrolysis temperature, 350 °C and 400 °C. This difference is due to the nature of hardwood lignins which contain mainly syringol type lignins [11]. Higher the pyrolysis temperatures, lower is the ratio S/G. Either the increase of pyrolysis temperatures promote the repolymerisation of syringol type lignins [16]. The lignin transformed by PHWT seems to be more thermally resistant and therefore less syringyl derivatives are produced. Or the increase of pyrolysis temperature might favor the degradation of syringyl lignins to light volatiles products (Fig. 3).

Besides, for these temperatures the pretreatment appears to favor the peak area%. The PHWT could weaken or break ether bonds to thus favor the subsequent thermal degradation of lignin [11]. The effect of PHWT on S/G ratio is particularly observable at low pyrolysis temperatures (Fig. 3). The decrease of S/G ratio for the pyrolysis products from PHWT aspen at highest severity, $S = 5.2$, could be explained by the partial solubilization of lignin during the PHWT (Table 1). The PHMT may have preferentially removed syringyl moieties.

3.2.2. *Fatty acids*

For the two wood species, the main fatty acids identified in pyrolysis products are hexadecanoic and octadecanoic acid as shown in Fig. 1 and in Table 3 for trembling aspen. They are probably derived from wood extractives [23].

At a heating rate of 100 °C/min, the peak area% of fatty acids were determined to be substantial for the aspen vapors obtained at 350 °C (Table 4). However, their contents decrease quickly with the increase of pyrolysis temperature. Extractives are thermally unstable and decompose completely at low temperatures [19,23]. On the other hand, the peak area% of fatty acids appears to not change much with pyrolysis temperature for spruce.

The peak area% of fatty acids obtained from the Py–GC/MS of spruce performed at heating rate of 1000 °C/min were higher than

Table 5
Composition of the pyrolysis products obtained at the heating rate of 1000 °C/min under different pyrolysis conditions from pretreated trembling aspen (TA) and from white spruce (WS) (average peak area% ± standard deviation%).

Temperature (°C)	Severity	Relative peak area ratio% ± SD%						
		Phenolics	Fatty Acids	Acids	Anhydrosugars	Furans	Ketones	Other
TA								
350	0	58.2 ± 4.0	11.6 ± 1.9	3.3 ± 0.9	3.4 ± 0.5	5.0 ± 1.0	1.4 ± 0.4	1.2 ± 0.0
	3.9	51.9 ± 5.9	9.5 ± 7.0	3.1 ± 0.8	3.0 ± 0.6	5.9 ± 1.6	2.3 ± 0.7	1.0 ± 0.6
	4.6	61.2 ± 4.6	4.9 ± 2.3	5.1 ± 1.1	3.2 ± 0.7	6.5 ± 0.6	2.0 ± 0.4	1.1 ± 0.5
	5.2	58.8 ± 6.1	11.4 ± 5.3	3.4 ± 1.8	2.6 ± 1.3	5.0 ± 1.2	0.9 ± 0.5	1.0 ± 0.4
400	0	53.0 ± 5.3	5.0 ± 0.3	5.9 ± 0.6	7.9 ± 0.9	7.4 ± 0.6	1.5 ± 0.3	1.5 ± 0.1
	3.9	49.4 ± 6.9	5.9 ± 3.8	5.5 ± 1.6	9.8 ± 3.4	8.1 ± 0.8	2.0 ± 0.7	1.3 ± 0.2
	4.6	50.2 ± 12.0	11.5 ± 2.6	4.2 ± 0.8	10.2 ± 5.7	5.8 ± 1.3	1.2 ± 0.2	1.0 ± 0.3
	5.2	42.5 ± 9.5	11.2 ± 6.1	2.5 ± 1.0	19.0 ± 6.7	5.8 ± 0.7	1.0 ± 0.4	0.9 ± 0.4
450	0	38.5 ± 7.2	13.9 ± 10.6	5.4 ± 0.6	12.3 ± 2.7	6.1 ± 0.5	1.0 ± 0.1	1.1 ± 0.0
	3.9	42.7 ± 8.0	12.1 ± 7.0	5.3 ± 0.8	11.6 ± 3.3	7.5 ± 1.2	1.8 ± 0.4	1.3 ± 0.3
	4.6	49.7 ± 4.8	8.1 ± 5.4	4.8 ± 1.1	12.8 ± 5.3	6.8 ± 1.2	1.3 ± 0.3	1.0 ± 0.2
	5.2	43.3 ± 9.1	5.8 ± 3.0	2.7 ± 0.8	21.7 ± 6.4	5.4 ± 0.5	0.7 ± 0.8	0.8 ± 0.4
500	0	37.1 ± 3.4	12.0 ± 6.5	4.8 ± 0.5	11.5 ± 1.7	5.0 ± 0.1	3.4 ± 1.6	1.0 ± 0.2
	3.9	32.1 ± 2.6	13.7 ± 6.2	4.9 ± 0.4	12.8 ± 1.9	6.7 ± 0.5	3.6 ± 0.4	1.5 ± 0.2
	4.6	34.8 ± 2.6	5.4 ± 1.5	4.0 ± 0.9	17.7 ± 1.2	7.3 ± 0.5	3.0 ± 0.3	1.3 ± 0.3
	5.2	30.5 ± 3.0	8.5 ± 4.2	3.0 ± 1.3	20.6 ± 3.4	6.2 ± 0.7	3.2 ± 1.0	1.4 ± 0.4
WS								
400	0	35.6 ± 6.3	20.6 ± 8.0	1.1 ± 0.5	10.6 ± 1.2	5.8 ± 1.1	1.0 ± 0.6	1.3 ± 0.2
	3.9	41.5 ± 8.0	12.0 ± 9.4	1.2 ± 0.3	12.6 ± 3.4	7.0 ± 1.7	1.7 ± 0.4	1.9 ± 0.6
	4.6	38.5 ± 11.0	21.1 ± 14.0	1.2 ± 0.3	11.3 ± 4.2	5.8 ± 2.0	1.7 ± 0.9	1.4 ± 0.6
	5.2	36.6 ± 9.5	28.5 ± 16.9	0.6 ± 0.2	8.7 ± 3.8	5.2 ± 2.1	1.4 ± 0.5	1.2 ± 0.6
450	0	32.1 ± 5.0	15.9 ± 15.9	2.4 ± 1.2	13.5 ± 4.6	6.8 ± 1.7	2.8 ± 0.3	2.0 ± 0.5
	3.9	34.6 ± 5.0	11.8 ± 5.5	1.8 ± 0.5	18.8 ± 1.5	7.8 ± 1.6	2.0 ± 0.3	2.0 ± 0.5
	4.6	40.4 ± 4.8	5.9 ± 2.3	1.3 ± 0.4	16.9 ± 4.1	8.6 ± 1.5	1.8 ± 0.3	2.4 ± 0.8
	5.2	45.9 ± 5.5	8.5 ± 2.7	0.4 ± 0.2	15.7 ± 2.6	6.0 ± 1.3	1.1 ± 0.1	1.7 ± 0.4
500	0	35.6 ± 3.8	20.8 ± 3.1	1.5 ± 1.0	14.5 ± 0.3	5.9 ± 0.6	1.8 ± 1.1	1.7 ± 0.5
	3.9	32.3 ± 7.3	16.1 ± 12.6	1.8 ± 0.4	18.8 ± 5.2	8.0 ± 2.5	2.2 ± 0.5	2.0 ± 0.7
	4.6	34.8 ± 4.0	6.7 ± 3.2	2.0 ± 0.6	18.5 ± 1.6	8.5 ± 0.9	2.3 ± 0.4	2.1 ± 0.3
	5.2	32.6 ± 4.4	11.6 ± 6.8	1.0 ± 0.6	20.4 ± 3.8	7.3 ± 0.6	2.1 ± 0.6	1.8 ± 0.2
550	0	36.8 ± 6.2	8.6 ± 1.5	2.8 ± 0.1	12.7 ± 0.9	9.0 ± 1.9	2.2 ± 0.4	1.9 ± 0.5
	3.9	32.7 ± 2.3	6.2 ± 3.0	3.0 ± 0.4	17.4 ± 2.6	8.2 ± 1.3	2.0 ± 0.2	2.1 ± 0.4
	4.6	34.0 ± 4.5	3.6 ± 1.3	2.4 ± 0.6	18.5 ± 2.5	7.9 ± 0.9	1.8 ± 0.3	1.9 ± 0.3
	5.2	31.9 ± 3.3	5.8 ± 4.3	1.6 ± 0.6	19.8 ± 1.3	7.5 ± 0.5	1.8 ± 0.3	1.8 ± 0.4

those obtained at 100 °C/min. To explain the large standard deviations, it should be recalled that the wood samples used for the Py–GC/MS analysis contained also bark, and that the content of extractives is usually more important in bark. Given the particle size used for the analytical pyrolysis, it is probable that examined samples had variable bark contents which could explain the variability of fatty acids production. The ANOVA analysis indicates that the pretreament have no effect on the peak area% of fatty acids for

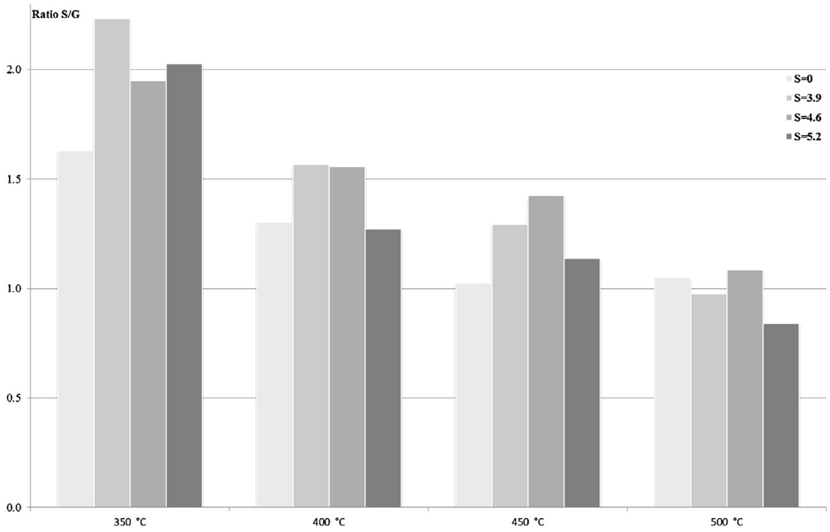

Fig. 3. Ratio S/G for PHWT trembling aspen (S = 0 – untreated; S = 3.9 pretreated at 175 °C; S = 4.6 at 195 °C and S = 5.2 at 215 °C) fast pyrolyzes performed at heating rate of 1000 °C/min and temperatures 350 °C, 400 °C, 450 °C and 500 °C.

aspen. Regarding spruce, the most significant effect on peak area% of fatty acids is that of pyrolysis temperature, particularly at 550 °C.

3.2.3. *Acids*

As can be seen from the results presented in Table 4, there is a very low production of low molecular weight acids and acid derivatives by pyrolysis performed at heating rate of 100 °C/min. Indeed, low molecular weight acids, mainly acetic acid, are only detected in aspen vapors at low pyrolysis temperature. Acid derivatives, such as propyl acetate, are also observed.

At heating rate of 1000 °C/min, the aliphatic and aromatic acids are identified among pyrolysis products from aspen. Acetic acid is the most important aliphatic, while benzoic and 4-hydroxybenzoic acid are the most important aromatic acids identified.

Acetic acid is derived mainly from the deacetylation of hemicelluloses [5,19]. Wood hemicelluloses are heteropolysaccharides composed mostly of glucomannans and xylans. There are more xylans in hardwood and more glucomannans in softwood. The acetyl groups are present in both mannan of softwoods and xylan of hardwoods but with higher frequency in hardwood xylans. In a previous study, it was demonstrated that, during pyrolysis, xylans are more degraded than glucomannans [23]. As shown in Table 1, hemicelluloses are eliminated by PHWT. Therefore, pretreated wood should give a peak area% of acids lower than untreated wood. The aromatic acids may be derived from lignins, as is the case for 4-hydroxybenzoic acid [24]. One should note that the other aromatic acids are also produced by pyrolysis, such as for example vanillic or syringic, but these were classified in this work rather among guaiacyl and syringyl derivatives.

For aspen, the peak area% of acetic acid is more important than that of aromatic acids, so it is assumed that the evolution of peak area% of acids could be resumed to acetic acid. According to the ANOVA analysis, only the pretreatment influences the acid peak area%. The results suggest that the higher the severity of the pretreatment, lesser would be the peak area% of acetic acid due to lower hemicelluloces content. However, the lower peak area% of acid, compared to untreated aspen, is determined only for aspen pretreated at $S = 5.2$. There are a number of possible explanations. One of them would be that some acetic acid produced by the pretreatment may have remained in the samples. Despite the 1 L water washing of each sample after PHWT, acetic acid could remain inside the structure of pretreated biomass. Acetic acid imprisoned in the biomass is then released during pyrolysis. Another hypothesis would be that the pretreatment may also favor the formation of acetic acid from pyrolytic pathways other than deacetylation of hemicelluloses.

In the case of softwood, low molecular weight acids identified after a pyrolysis performed at heating rate of 1000 °C/min consist mainly of acetic acid. There is less hemicellulose in softwood than in hardwood and also the acetylated mannan is just one of the softwood hemicelluloses, so the production of acetic acid should be inferior. The results for spruce, shown in Table 5 confirm this hypothesis. Despite their different hemicelluloses contents, as shown in Table 1, untreated spruce and pretreated spruce at $S = 3.9$ and $S = 4.6$ seem to produce approximately the same peak area% of acids by pyrolysis performed at high heating rate. As discussed for aspen, it seems that the pretreatment may favor the formation of acetic acid by alternative pyrolytic pathways. However, it is noteworthy that for the samples pretreated at the highest $S = 5.2$, in which all hemicelluloses are supposed to be removed from both aspen and spruce, the peak area% of acids are generally lower than those obtained for untreated woods or from those treated at lower severities (Table 5).

The pretreatment seems to have two types of effects on two studied wood species. On one hand, PHWT at severities of $S = 3.9$ and $S = 4.6$ seem to have no effect on the peak area% of acids in pyrolysis products as it remained almost the same as that for untreated wood, despite the fact that hemicelluloses are progressively removed from wood upon PHWT. The formation of acetic acid from cracking of lignin side-chains or from the fragmentation of cellulose [19] may be favored by PHWT. On the other hand, pyrolysis of woods pretreated at the highest $S = 5.2$ yields lower peak area% of acid in agreement with the removal of hemicelluloses.

3.2.4. *Anhydrosugars*

Anhydrosugars are derived from thermal degradation of holocellulose. The pyrolytic pathway is similar for cellulose and hemicelluloses but most of anhydrosugars are produced from cellulose. First, cellulose is degraded to an “active” form. This “active cellulose” is then depolymerised by random cleavage of glycosidic linkages to form mono and oligosaccharides [11]. During this final step, competitive reactions may occur. The fragmentation reaction would form small carbonyl bearing molecules, such as the hydroxyacetaldehyde.

At heating rate of 100 °C/min, the peak area% of anhydrosugars is lower for aspen than for spruce. Furthermore, it seems that the anhydrosugar peak area% increase with the increase of PHWT severity particularly so at pyrolysis temperatures of 500 °C for aspen and at 500 °C and 550 °C for spruce. In the case of softwood, the phenomenon is most significant for the severity factor 5.2 (Table 4).

The peak area% of anhydrosugar increased significantly when Py–GC/MS is performed at high heating rate of 1000 °C/min (Table 5). At this high heating rate, levoglucosan (1,6-anhydro-β-glucopyranose) is identified as the major anhydrosugar. Hence, the peak area% of anhydrosugar could be assimilated to the peak area% of levoglucosan. The standard deviations are large because the peak corresponding to levoglucosan is wide. Indeed, levoglucosan is released by GC/MS at the same time as some depolymerization products with similar structures. Peaks of some pyrolytic products may thus overlap one of the levoglucosan on the total ion current as presented in Fig. 1.

For both hardwood and softwood, the peak area% of levoglucosan is more sensitive to the severity of the pretreatment than to the pyrolysis temperature. In the case of aspen, the influence of PHWT high severity of $S = 5.2$ is particularly noticeable from 400 °C and the effect of PHWT severity of $S = 4.6$ from 500 °C. Aspen pretreated at $S = 5.2$ was determined to have the highest cellulose contents of all studied samples, as shown in Table 1, which could explain the high peak area% of levoglucosan in pyrolysis products originating from that sample. For softwood, levoglucosan can be derived from both cellulose and mannan. Indeed, softwood hemicelluloses have a significant content of hexosans – (galacto) glucomannans. The effect of PHWT on levoglucosan peak area% is different for spruce and aspen. It appears that PHWT increase the peak area% of levoglucosan in pyrolysis products regardless of the severity of the pretreatment. Even at $S = 5.2$ when almost all hemicelluloses were removed from the biomass and thus levoglucosan was therefore no longer produced from glucomannans, the peak area% of levoglucosan was comparable to those obtained for the others severities. This may indicate that levoglucosan is predominantly produced from cellulose. For both species, the pretreatment seems to enhance the formation of levoglucosan. PHWT alters cellulose structure and favors the formation of “active cellulose”. However, the results of this study indicate that PHWT do not have exactly the same effect on two studied species.

The results of our study seems to indicate that the peak area% of anhydrosugars had increased starting from pyrolysis temperature 450 °C confirming that levoglucosan formation is favored at elevated temperatures [21,23]. This phenomenon seems to be related to the acceleration of the glycosidic bond cleavage at high temperatures. For softwood, the production seems to slightly decrease

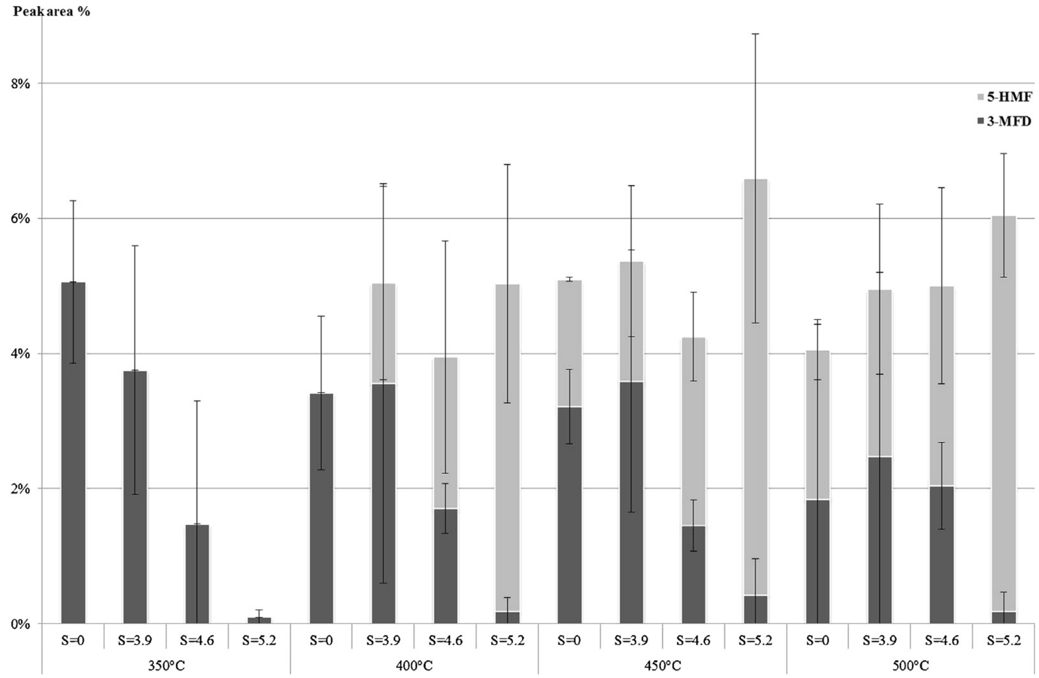

Fig. 4. Peak area% of 3-methyl-2,4(3H, 5H) furandione (3-MFD) and 5-hydroxymethyl-2-furancarboxaldehyde (5-HMF) for PHWT trembling aspen (*S* = 0 – untreated; *S* = 3.9 pretreated at 175 °C; *S* = 4.6 at 195 °C and *S* = 5.2 at 215 °C) fast pyrolyzes performed at heating rate of 100 °C/min and temperatures 350 °C, 400 °C, 450 °C and 500 °C.

at 550 °C. Too high pyrolysis temperature seems to promote secondary reactions of anhydrosugars and thus enhance competing pyrolysis reactions [25].

3.2.5. Furans

Furans are derived from thermal degradation of holocellulose [23].

For a pyrolysis performed at heating rate of 100 °C/min, two majors furanic compounds are identified in aspen pyrolysis products, 3-methyl-2,4(3H, 5H) furandione (3-MFD) and 5-hydroxymethyl-2-furancarboxaldehyde (5-HMF). The peak area% of furans can be therefore assimilated to the production of these two pyrolysis products for the pyrolysis performed at low heating rate. The results are shown in Fig. 4.

The pretreatment does not seem to have the same effect on the production of the two furans. Indeed, the peak area% of 3-MFD decreased with the increase of PHWT severity whereas that of 5-HMF increased. This phenomenon is particularly pronounced for high severity factor *S* = 5.2. Besides, the formation of 5-HMF is shifted to lower pyrolysis temperatures for the pretreated wood. The pyrolysis temperature of 350 °C seems to be too low for the formation of 5-HMF so the peak area% of furans decreased at this pyrolysis temperature with the increase of pretreatment severity. Beyond 400 °C, the decrease of peak area% of 3-MFD is offset by the increase of peak area% of 5-HMF. Therefore, the peak area% of furans remained relatively unchanged between the different severities as shown in Table 4. Regarding spruce, the main furanic compound is 5-HMF with the exception of the pyrolysis performed at 400 °C where 3-MFD is also significant. The peak area% of furanic compounds could be assimilated to the peak area% 5-HMF. As it was observed for aspen, the peak area% of 5-HMF is affected by PHWT but the higher effect of PHWT was only observable at 400 °C and 450 °C for the severity of *S* = 5.2. 5-HMF is a product of the thermal degradation of cellulose [19,23]. At low heating rate, 100 °C/min, instead of favor the formation of levoglucosan, it is suggested that the pretreatment promote the production of 5-HMF by altering the structure of cellulose.

The composition of furanic compounds from pyrolysis at 1000 °C/min is much more complex than from pyrolysis at 100 °C/min. The high heating rate allows the formation of light furans such as furfural, furanmethanol and furanone. Therefore, the peak area% of furans cannot be assimilated to the peak area% of 3-MFD or of 5-HMF. Although the increase of pretreatment severity induces the removal of hemicelluloses, the effect of PHWT severity on furans peak area% is barely noticeable for both aspen and spruce.

3.2.6. Ratio carbohydrates/lignins derivatives

In addition to acids, anhydrosugars and furans, the others carbohydrates derived compounds identified were identified: pyrans, ketones, aldehydes and alcohols. As presented in Table 4, for the pyrolysis performed at a heating rate of 100 °C/min, pyrans are only identified in the pyrolysis products from aspen and the last column, named other, regroups ketones, aldehydes and alcohols. At 1000 °C/min, Table 5, the peak area% of pyrans are so low, under 1.5%, that they are regrouped with the aldehydes and alcohol in the “other” section.

To observe the effect of pretreatment and pyrolysis temperature on a more general level, a ratio between the total peak area% of carbohydrates and the total peak area% of lignins derivatives (ratio C/LD) was calculated. The results for the Py–GC/MS performed at a heating rate of 100 °C/min and 1000 °C/min are presented in Figs. 5 and 6, respectively.

The results obtained for pyrolysis performed at 100 °C/min, confirm the predominance of phenolics. The influence of PHWT is more clearly observable and it is particularly from the case of 500 °C for aspen and from 450 °C for spruce (Fig. 5). At 1000 °C/min, the ratio C/LG was always more important that the ratio at 100 °C/min (Fig. 6). High heating rate seems to allow a more pronounced thermal degradation of cellulose, thus favors the production of levoglucosan. Moreover, like for heating rate of 100 °C/min, the ratio C/LD shows that the pretreatment has more effect from 500 °C for both hardwood and softwood. Thus, the influence of PHWT on ratio C/LD seems to be intensified by high pyrolysis temperatures.

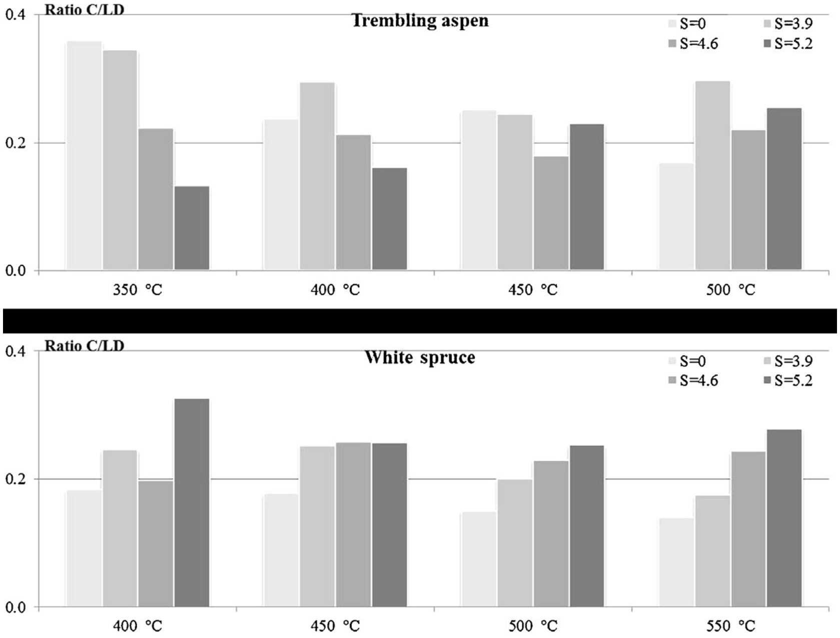

Fig. 5. Ratio carbohydrates/lignin (C/LD) for PHWT trembling aspen ($S = 0$ – untreated; $S = 3.9$ pretreated at 175 °C; $S = 4.6$ at 195 °C and $S = 5.2$ at 215 °C) fast pyrolyzes performed at heating rate of 100 °C/min and temperatures 350 °C, 400 °C, 450 °C and 500 °C and for PHWT white spruce performed at the same rate and temperatures 400 °C, 450 °C, 500 °C and 550 °C.

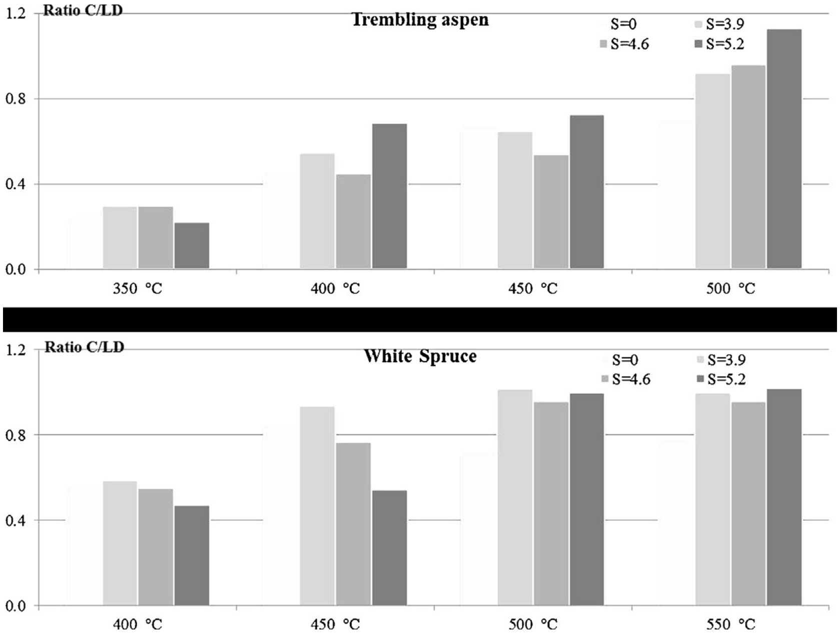

Fig. 6. Ratio carbohydrates/lignin (C/LD) for PHWT trembling aspen ($S = 0$ – untreated; $S = 3.9$ pretreated at 175 °C; $S = 4.6$ at 195 °C and $S = 5.2$ at 215 °C) fast pyrolyzes performed at rate of 1000 °C/min and temperatures 350 °C, 400 °C, 450 °C and 500 °C and for PHWT white spruce performed at the same rate and temperatures 400 °C, 450 °C, 500 °C and 550 °C.

4. Conclusions

In this study, an analytical pyrolysis was performed on woody biomass, trembling aspen and white spruce, previously pretreated by a PHWT process. The pretreatment caused a chemical modification of biomass. Py–GC/MS was applied at two heating rates, 100 °C/min and 1000 °C/min and temperatures varying between 350 °C and 550 °C, to simulate a fast pyrolysis process. Py–GC/MS was applied as an analytical technique since it allowed the investigation of the influence of the alterations caused by PHWT on the composition of pyrolysis products.

It has been shown that a high heating rate promoted the yield of pyrolysis products. Thus, to obtain a high bio-oil yield, our results suggest the fast pyrolysis process should be performed at high heating rate also. The constituents of pyrolysis products were classified in eleven chemical categories: phenolics including syringyl, guaiacyl, and other aromatic moieties, anhydrosugars, low molecular weight acids, fatty acids, furans, pyrans, ketones, aldehydes and alcohols. The major compounds identified in pyrolysis products obtained from pretreated samples of both aspen and spruce at low heating rate were phenolics followed by furans. Low molecular weight acids were barely present. At high heating rate, phenolics were also the major components for both wood species but their peak area% were much lower whereas the peak area% of anhydrosugars issued from pyrolysis increased significantly. The analysis revealed the presence of low molecular weight acids, mainly acetic acid, in pyrolysis products were more produced at high heating rate. Moreover it was shown that the acids remain still important in the composition of pyrolysis products even in the pyrolysis organic condensable products produced from the wood which had been pretreated. It could be explained by either their remaining in the pretreated samples or by alternative pathways of their generation through pyrolysis.

The Py–GC/MS analytical technique was demonstrated to not only help anticipate the chemical composition and the yield of the bio-oil to be produced from the pretreated wood but also to contribute to the creation of a substantial database of wood pyrolysis compounds and thus indicate to the potential of their new applications.

Acknowledgements

This research was supported by funding from the Consortium de Recherche et Innovations en Bioprocédés Industriels au Québec (CRIBIQ), UNIBOARD Inc. usine Sayabec and Coopérative Forestière de la Matapédia (CFM), and by the Natural Sciences and Engineering Research Council of Canada (NSERC). The authors would also like to thank Groupe BSL for supplying the forest biomasses. Special thanks to Yves Bédard for his technical assistance and to Claudia Caceres for her help on ANOVA analysis.

References

[1] International Energy Agency, Key World Energy Statistics, 2012.

[2] F. Carvalheiro, L.C. Duarte, F.M. Girio, Hemicellulose biorefineries: a review on biomass pretreatments, J. Sci. Ind. Res. 67 (2008) 849–864.

[3] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass Bioenergy 38 (2012) 68–94.

[4] D. Meier, B. van de Beld, A.V. Bridgwater, D.C. Elliott, A. Oasmaa, F. Preto, State-of-the-art of fast pyrolysis in IEA bioenergy member countries, Renew. Sustain. Energy Rev. 20 (2013) 619–641.

[5] D. Mohan, C.U. Pittman Jr., P.H. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review, Energy Fuels 20 (2006) 848–889.

[6] C. Branca, P. Giudicianni, C. Di Blasi, GC/MS characterization of liquids generated from low-temperature pyrolysis of wood, Ind. Eng. Chem. Res. 42 (2003) 3190–3202.

[7] E.M. Hassan, F. Yu, L. Ingram, P. Steele, The potential use of whole-tree biomass for bio-oil fuels, Energy Sources Part A: Recovery Util. Environ. Effects 31 (2009) 1829–1839.

[8] R.A. Hague, The Pre-treatment and Pyrolysis of Biomass for the Production of Liquids for Fuels and Speciality Chemicals, Aston University, 1998.

[9] J. Meng, J. Park, D. Tilotta, S. Park, The effect of torrefaction on the chemistry of fast-pyrolysis bio-oil, Bioresour. Technol. 111 (2012) 439–446.

[10] E. Le Roux, P.N. Diouf, T. Stevanovic, Characterization of the properties of thermally pre-treated forest biomass, J. Sci. Technol. For. Prod. Process. 2 (2012) 33–37.

[11] J. Grinins, B. Andersons, V. Biziks, I. Andersone, G. Dobele, Analytical pyrolysis as an instrument to study the chemical transformations of hydrothermally modified wood, J. Anal. Appl. Pyrolysis 103 (2013) 36–41.

[12] R.L. Johnson, S.-S. Liaw, M. Garcia-Perez, S. Ha, S.S.-Y. Lin, A.G. McDonald, et al., Pyrolysis gas chromatography mass spectrometry studies to evaluate high-temperature aqueous pretreatment as a way to modify the composition of bio-oil from fast pyrolysis of wheat straw, Energy Fuels 23 (2009) 6242–6252.

[13] R.P. Overend, E. Chornet, J.A. Gascoigne, Fractionation of lignocellulosics by steam-aqueous pretreatments, Philos. Trans. R. Soc. A: Math. Phys. Eng. Sci. 321 (1987) 523–536.

[14] N. Abatzoglou, E. Chornet, K. Belkacemi, R.P. Overend, Phenomenological kinetics of complex systems: the development of a generalized severity parameter and its application to lignocellulosics fractionation, Chem. Eng. Sci. 47 (1992) 1109–1122.

[15] J. Ralph, R.D. Hatfield, Pyrolysis–GC–MS characterization of forage materials, J. Agric. Food Chem. 39 (1991) 1426–1437.

[16] M.F. Nonier, N. Vivas, N.V. de Gaulejac, C. Absalon, P. Soulié, E. Fouquet, Pyrolysis–gas chromatography/mass spectrometry of *Quercus* sp. wood: application to structural elucidation of macromolecules and aromatic profiles of different species, J. Anal. Appl. Pyrolysis 75 (2006) 181–193.

[17] M. Arias, O. Polvillo, J. Rodriguez, M. Hernandez, J. Gonzalez-Perez, F. Gonzalez-Vila, Thermal transformations of pine wood components under pyrolysis/gas chromatography/mass spectrometry conditions, J. Anal. Appl. Pyrolysis 77 (2006) 63–67.

[18] A. Fivga, Comparison of the Effect of Pre-treatment and Catalysts on Liquid Quality from Fast Pyrolysis of Biomass, Aston University, 2011.

[19] C. Dong, Z. Zhang, Q. Lu, Y. Yang, Characteristics and mechanism study of analytical fast pyrolysis of poplar wood, Energy Convers. Manag. 57 (2012) 49–59.

[20] B. Zhang, Z. Zhong, K. Ding, Y. Cao, Z. Liu, Catalytic upgrading of corn stalk fast pyrolysis vapors with fresh and hydrothermally treated HZSM-5 catalysts using Py–GC/MS, Ind. Eng. Chem. Res. 53 (2014) 9979–9984.

[21] S. Thangalazhy-Gopakumar, S. Adhikari, R.B. Gupta, S.D. Fernando, Influence of pyrolysis operating conditions on bio-oil components: a microscale study in a pyroprobe, Energy Fuels 25 (2011) 1191–1199.

[22] A. Heigenmoser, R. Fuchs, E. Windeisen, G. Wegener, Characterization of different wood samples using a new combined method of evolved gas analysis and pyrolysis–gas chromatography/mass spectrometry, Wood Sci. Technol. 46 (2012) 637–642.

[23] R. Alen, E. Kuoppala, P. Oesch, Formation of the main degradation compound groups from wood and its components during pyrolysis, J. Anal. Appl. Pyrolysis 36 (1996) 137–148.

[24] O. Faix, D. Meier, I. Fortmann, Thermal-degradation products of wood – gas-chromatographic separation and mass-spectrometric characterization of monomeric lignin derived products, Holz Als Roh-Werkst. 48 (1990) 281–285.

[25] F. Shafizadeh, Introduction to pyrolysis of biomass, J. Anal. Appl. Pyrolysis 3 (1982) 283–305.